

VOLATILIZATION OF PCBs DURING PLANNED
WAUKEGAN HARBOR CLEANUP OPERATIONS

LITERATURE REVIEW

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EXECUTIVE SUMMARY

Potential polychlorinated biphenyl (PCB) volatilization to the atmosphere during Waukegan Harbor cleanup operations is reviewed in this study report.

Atmospheric transport is the major mode of global dispersal of PCBs, according to the literature. One researcher has estimated 1.3 to 1.8×10^6 kg/year (7,800 to 10,000 lbs./day) discharge to the air from all North American sources (early 1970's). Mason and Hanger estimates, using data obtained by General Electric in a test tank in New York state, that several pounds per day could be volatilized when the most contaminated Waukegan Harbor sediments are dredged and placed in the proposed lagoon for settling.

PCB volatilization rates are difficult to predict. Published literature values on volatilization rates, Henry's law constants and solubility of PCB in water, may differ by an order of magnitude even comparing the same Aroclor at the same temperature. The reasons for these disagreements are discussed in this report. Mason & Hanger recommends monitoring of PCB concentrations in air and water during all phases of the operation.

To minimize volatilization, the most contaminated sediments should be placed in a special compartment in the proposed lagoon. Dredging should begin with the more contaminated sediments being dredged first. The

less contaminated sediments when dredged will form a cap to minimize volatilization of PCBs from more contaminated sediments. Finally, when dredging is finished and excess water drawn off and treated, a dust control emulsion formulation should be sprayed onto exposed sediment which has been placed in the lagoon. Small areas of lagoon sediment should be excavated at a time to minimize volatilization when the contaminated material is transported to an approved landfill.

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1.0 INTRODUCTION

Mason & Hanger-Silas Mason Co., Inc. (Mason & Hanger) was engaged by the U.S. EPA (U.S. EPA Environmental Emergency Response Unit Contract 68-03-2647) to prepare plans and specifications for cleanup of polychlorinated biphenyl contamination in Waukegan Harbor, Waukegan, Illinois. The contamination resulted when one of the local industries allowed PCB's to discharge via an outfall in Slip #3 of Waukegan Harbor during an approximate 20 year period. Mason & Hanger has estimated that approximately 168,000 cubic yards of Waukegan Harbor bottom sediments will have to be removed to clean up areas of contamination greater than 10 parts per million PCB, or 48,000 cubic yards of sediments greater than 50 parts per million PCB.

The plans and specifications for Waukegan Harbor cleanup call for:

- (1) construction of one or two lagoons each of approximately 150,000 cubic yard capacity;
- (2) dredging of Waukegan Harbor and placing the dredged material in the lagoon(s),
- (3) dewatering the dredged sediments in the lagoon(s),
- (4) return of the dredge slurry water back to the Harbor after treatment for removal of PCBs,

- (5) excavation of a small area of deep contamination at the old Slip #3 outfall,
- (6) treatment of rain water and lagoon leachate water,
- (7) final excavation of the lagoon contents for burial in a landfill approved for PCBs, and
- (8) removal of the lagoon(s) and land restoration.

The availability and timing of the necessary funding to complete these operations dictate whether 48,000 cubic yards (Over 50 ppm of PCB) or 168,000 cubic yards (Over 10 ppm PCB) of sediments will be removed and whether one or two lagoons will be constructed. The plans and specifications are contingent upon vacant land owned by the Outboard Marine Corporation adjacent to Waukegan Harbor being available for lagoon construction. Current scheduling calls for construction of one lagoon on this land during 1981, followed by dredging 48,000 cubic yards (contamination over 50 ppm PCB) of sediments in 1982, including dewatering and return of the treated water back to the Harbor. If funding is available, a second lagoon may be constructed (or the first lagoon dredge spoils removed and the lagoon used again) for removal of the rest of the contaminated sediments in Waukegan Harbor.

All of these operations will result in transfer of some PCBs to the air. PCB transfer can occur due to volatilization from water and dredged

sediments and due to fugitive dust carried into the atmosphere by wind.

The U.S. EPA requested that Mason & Hanger review this problem and incorporate appropriate control measures into the plans and specifications for dredging, dewatering, and final excavation.

2.0 LITERATURE REVIEW - VOLATILIZATION OF PCBs AND OTHER CHLORINATED AROMATIC HYDROCARBONS

2.1 Dispersal of PCBs and Other Hydrocarbons in the Atmosphere

2.1.1 Role of Volatilization on Dispersal of PCBs in the Environment

There is general agreement (Mackay, 1973) that atmospheric transport is the major mode of global dispersal of chlorinated aromatic hydrocarbons such as pesticides and polychlorinated byphenyls (PCBs). Pesticide and PCBs have been found in ice collected in Arctic and Antarctic regions. The hydrocarbons volatilize into the atmosphere and can be carried thousands of miles from the original source either as a vapor or adsorbed onto dust particles. Some of these materials such as pesticide are applied by spraying techniques with the possibility of direct evaporation. Some are dispersed during incineration. However, most transfer is believed to take place under ambient conditions as the result of natural evaporative processes from soils, landfills, water or locations where the hydrocarbon is used.

Evaporation of chlorinated aromatic hydrocarbons from water under ambient conditions is surprisingly high despite the low vapor pressure (often less than 10^{-6} atm). The reason is that these compounds have high activity coefficients in water which result in high equilibrium vapor partial pressures in water and thus high rates of

volatilization (Mackay, 1973). These compounds have a low water solubility and are strongly hydrophobic, and tend to partition themselves into the air or adsorb onto solids which may be introduced into the water.

Various researchers have measured concentration of PCBs in the air. Table 1 shows values on the order of 1 to 10 nanograms per cubic meter (ng/m^3) when air is sampled above land and values in the order of 0.1 to 2 ng/m^3 when air is sampled above larger expanses of water. Vent gas emitting from an ordinary landfill site near Chicago contained 3240 ng/m^3 (3.24×10^{-6} grams/meter³) of PCB. The New York Department of Environmental Conservation sampled the air above the uncontrolled Caputo dump site north of Albany, New York shortly after it was discovered in 1976 and found 300,000 ng/m^3 (3×10^{-4} grams/cubic meter) of PCB. The Caputo site was since capped with manure, papermill sludge, and top soil to minimize volatilization. By comparison, the OSHA recommended standard for maximum worker exposure to Aroclor 1242 is 1000 $\mu\text{g}/\text{m}^3$ (micrograms per cubic meter) in the air at any time. The National Institute of Occupational Safety and Health recommends that a worker not be exposed to more than 1 $\mu\text{g}/\text{m}^3$ in the air during an eight hour period. Dr. Hayley of the New York Department of Environmental Conservation recommends (1979) that a worker should not be exposed to more than 3 μg PCB per kg of body weight per day; for example, this calculates to a maximum exposure of 13 $\mu\text{g}/\text{m}^3$ for a 70 kg man breathing 15 cubic meters of air during an eight hour period.

2.1.2 Dry Deposition of PCBs from the Atmosphere

Eisenreich (2), Murphy (9), McClure (30) and most other researchers agree that atmospheric PCBs generally originate from land-

based sources, especially near metropolitan areas and from dumps and as the result of incineration. There may be significant dry deposition of PCBs onto the land within several miles of the source. Most of the PCBs are scrubbed out of the atmosphere during precipitation events. Eisenreich (2), Murphy (9), and Bidleman (3) agree that there is a net transfer of PCBs from the atmosphere to large bodies of water, mostly occurring during precipitation events.

McClure (30), measuring atmospheric PCB concentration and deposition at LaJolla, California, concluded that most dry deposition of aerosol PCB introduced into the air occurred within 10 KM of a source (Los Angeles landfill; contributions from several sources such as fires and weathering of products containing PCBs). His dry depositions measurements yielded values ranging from 2×10^{-9} to 9×10^{-7} (average: 3×10^{-7}) grams/ meter²/day of PCB. The general source was located by correlating these PCB measurements with windspeed and direction. Deposition was measured by allowing PCB aerosol droplets and particles to deposit on mineral oil-coated glass deposition plates, and analyzing the mineral oil for PCBs. McClure estimated a half life of the PCB aerosols in the atmosphere about 5 hours. The PCB source strength was estimated to be about 20 or 30 metric tons per year (1972 data). Dry deposition rather than deposition during rainfall accounted for the majority of PCB fallout at this southern California location.

Stratton (31) surveyed environmental contamination near the Monsanto Co. PCB manufacturing facility in Sauget, Illinois and two

industrial PCB use areas located in urban Chicago and suburban Detroit. The distribution of PCBs in the soil near the facilities suggested an airborne mode of transport from the source. Stratton did not comment whether the majority of PCBs were scrubbed out of the air during rainstorms or whether dry deposition of PCBs occurred. Probably, most of the PCBs were deposited on surrounding soils as the result of dry deposition of aerosols or particles.

Tofflemire (1) reported on PCB contamination in vegetation near several PCB dump sites in New York, including the Ft. Miller Dump, Caputo Dump, and Moreau dredge site. The plants, especially the leaves or needles on trees and certain species such as goldenrod, contained high PCB levels compared with plants remote from the site. The PCB concentrations in the plants decreased rapidly from the site. Plants upslope but downwind from the site were elevated in PCBs indicating that air, not water, was the source of the PCB transport.

Measurements (Table 2) of the rate of dry deposition of PCB from the air yielded values generally over $1,000 \text{ ng/m}^2/\text{day}$ if near a source of PCB volatilization and generally less than $500 \text{ ng/m}^2/\text{day}$ if remote from areas of significant volatilization.

Clifford Rice of the University of Michigan measured dry deposition of PCB at Waukegan Harbor on April 29, 1980, obtaining values of 400 and 204 ng/m^2 over two 6 hour periods. The PCB pattern most resembled Aroclor 1248. The average of the two values was 302 ng/m^2 for 6 hours or $1208 \text{ ng/m}^2/\text{day}$. This is equivalent to 2.5 pounds

per square mile per year.

2.1.3 PCBs in Precipitation

Murphy (9) measured concentrations of PCB in rain and snow (Table 2) collected at various locations near or at Lake Michigan. He found that PCBs in precipitation samples contained more than 20 percent Aroclor 1260 whereas PCBs in air samples contained about 3 percent Aroclor 1260. Murphy argued that air particulates contained Aroclor 1260, and that these air particulates were being scrubbed from the air during precipitation events. A mass balance based on Aroclor 1260 suggested that only 15 percent of the PCBs in the atmosphere at Lake Michigan are on particulates and the rest of the PCBs are present as vapor. PCB in air samples collected were on the average 84 percent Aroclor 1242. Murphy commented that the dry collecting method used by McClure (30) at La Jolla should scavage both PCB vapor and particulates (aerosols) and not just particles as McClure implied. McClure did not consider the Aroclor distribution in his measurements of PCB in the air and dry deposition.

Murphy (9) estimated the total amount of deposition of PCBs into Lake Michigan from precipitation was 4800 kg/year. This estimation is based on a weighted mean of 35 measurements at Chicago and Beaver Island of 111 ng/l, a lake area of 58,000 km², and a mean precipitation of 740 mm/year:

$$\frac{111 \text{ ng}}{\text{liter}} \frac{\text{kg}}{10^{12} \text{ ng}} \frac{740 \text{ mm}}{\text{year}} (58,000 \text{ km}^2) \frac{10^{12} \text{ mm}^2}{\text{km}^2} \frac{\text{liter}}{10^6 \text{ mm}^3} = 4764 \text{ kg/yr}$$

This number is equivalent to about 0.5 pounds per square mile per year. In addition to PCBs in precipitation, there would be some dry deposition of PCBs into Lake Michigan. Murphy estimated that the dry deposition of PCBs into Lake Michigan could be on the order of 2500 kg/year (this number may include some unidentified industrial discharge of PCB). The 2500 kg/year disposition is equivalent to 0.25 lbs/square mile/year or 121 ng/m²/day. Murphy (9) found PCB concentration in rainwater collected at Chicago and Beaver Island (opposite ends of Lake Michigan) were not statistically significant. Table 2 data and work by McClure (30) indicated a correlation between dry deposition of PCB and distance from the PCB source.

2.1.4 Total Deposition of PCBs from Atmosphere

Bidleman (3) has estimated the flux of PCB and chlorinated pesticides (DDT) to an area of the North Atlantic Ocean of about $1 \times 10^7 \text{ km}^2$ centered about the Bermuda Rise, remote from any significant sources of these chemicals. The flux of PCB and DDT was due to a combination of (1) dry particulate deposition, (2) rain input, and (3) vapor phase transfer. Bidleman estimated, based on measurements of PCB in rainfall collected on dry deposition collectors, and PCB concentrations in Ocean water that the total flux of PCB to this part of the Atlantic Ocean was about $1.4 \times 10^5 \text{ kg/year}$ (equivalent to 0.008 pounds of PCB per square

mile per year). The flux of DDT to this part of the Atlantic Ocean was estimated to be 1.4×10^4 kg per year. Bidleman estimated that the 1.4×10^5 kg per year PCB input consisted of 6×10^4 kg/year from vapor phase transfer, 3×10^4 kg/year from particle deposition, and 5.2×10^4 kg/year from rainfall. Similar estimates were made for DDT.

Nisbet and Sarofim in 1972 (3) formulated a mass balance for PCB in the environment based on sales and estimated useful lives of PCB-containing products and estimated that 1.3 to 1.8×10^6 kg/year of PCBs are discharged into the atmosphere each year from North America by vaporization and burning.

Eisenreich (2) (13) (27) estimated the rate of dry deposition and wet deposition (with precipitation events) of PCB and chlorinated pesticides to the Great Lakes. Eisenreich estimated that 3,000 to 6,000 kg/year of PCBs fall on Lake Superior during rain and snowfalls (calculation based on 30 to 100 ng/l PCB in rainfall, a lake area of 8.21×10^{10} square meters, and rainfall totaling 0.8 meters per year). Eisenreich also assumed that 90 percent of the atmospheric PCBs was in the vapor phase and 10 percent of the atmospheric PCBs was particulate and also calculated a vapor phase and particulate distribution to Lake Superior. His calculations are as follows:

PCBs in Rainfall to Lake Superior

$$30 \frac{\text{ng}}{\text{liter}} \times 8.21 \times 10^{10} \text{ m}^2 \times (0.8 \text{ m}) \times \frac{(10)^3 \text{ liter}}{\text{m}} \times \frac{\text{kg}}{10^{12} \text{ ng}} = 2000 \text{ kg/year}$$

PCBs to Lake Superior due to Dry Deposition

$$\text{Deposition Rate} = V_d C \quad (\text{Area})$$

V_d = deposition velocity, 0.3 meters/sec.

$C = 1.0 \text{ ng/m}^3$ total PCB, of which 10 percent was assumed to be particulate

$$\begin{aligned} \text{Deposition Rate} &= (0.3 \text{ cm/sec}) \times (1 \times 10^{-9} \text{ g/m}^3) \times (3.15 \times 10^7 \\ &\quad \text{sec/y}) \times (10^{-3} \text{ kg/g} \times (0.1) \times 8.21 \times 10^{10} \text{ m}^2 = \\ &\quad 7800 \text{ kg/year} \end{aligned}$$

PCBs to Lake Superior by Vapor Phase Exchange

$$\text{Flux} = K_{OL} C$$

K_{OL} = mass transfer coefficient

$K_{OL} = 0.008 \text{ cm/sec}$ for wind speed of 3 to 10 m/sec. (from Figure 6 of Cohen's paper) page 556 of Environmental Science Technology, May 1978).

$C = 90 \text{ percent of } 1.0 \text{ ng/m}^3$

$$\text{Flux} = 0.008 (0.9) (1.0) (3.15 \times 10^7) (10)^{-2}$$

$$\text{Flux} = 2300 \text{ ng/m}^2/\text{year}$$

$$\text{Gaseous input} = (2300) (8.21 \times 10^{10}) (10)^{-12} = 200 \text{ kg/year}$$

PCBs to Lake Superior due to Dry Deposition

$$\text{Deposition Rate} = V_d C \quad (\text{Area})$$

V_d = deposition velocity, 3 meters/sec.

$C = 1.0 \text{ ng/m}^3$, total PCB of which 10 percent was assumed to be particulate.

Total PCB input to Lake Superior = $200 + 7800 + 2000 = 10,000$ kg/year.

This number of 10,000 kg/year is equivalent to 0.7 pounds of PCB per square mile per year.

Eisenreich (2) also published estimates of PCB and other chlorinated organics to each of the other Great Lakes. The total input of PCB was as follows:

| | |
|---------------|----------------|
| Lake Superior | 10,000 kg/year |
| Lake Michigan | 6,900 kg/year |
| Lake Huron | 7,200 kg/year |
| Lake Erie | 3,100 kg/year |
| Lake Ontario | 2,300 kg/year |

The estimate of 6,900 kg/year total for Lake Michigan is in the same order of magnitude as Murphy's estimate of 4,800 kg/year from rainfall and 2,500 kg/year from dry deposition ($2500 + 4800 = 7300$ kg/year).

2.1.5 Summary

Volatilization of PCBs from land based sources is the major method of dispersal in the environment. The PCBs exist in the atmosphere both in particulate form (adsorbed onto particulates) and as

a free vapor. The PCBs are removed from the atmosphere by three mechanisms, namely: (1) scrubbing the air during precipitation events, (2) dry depositions of particulates especially near the source, and (3) vapor exchange of PCBs with bodies of water. The total amount of PCBs reaching Lake Michigan from atmospheric deposition is estimated to be 7000 kg/year (0.7 pounds per square mile per year).

TABLE 1
MEASUREMENTS OF CONCENTRATIONS OF PCB IN THE ATMOSPHERE

| <u>RESEARCHER</u> | <u>REFERENCE</u> | <u>SAMPLE DATE</u> | <u>LOCATION</u> | <u>PCB CONCENTRATION</u> |
|-------------------|------------------|-----------------------|----------------------------------|--------------------------------|
| Murphy | 9 | 1975-76 | DePaul Univ. Chicago, IL | 7.6 ng/m ³ |
| Murphy | 9 | Nov. 1975 | Mammoth Cave N.P., KY | 6.7 ng/m ³ |
| Rice | U.S. EPA | Apr 29 1980 | Public Dock, Waukegan Harbor, IL | 12.45 ng/m ³ |
| McClure | 30 | Mar-Apr 1973 | La Jolla, Calif. | 0.45 to 14 ng/m ³ |
| Harvey | 13 | 1973? | Mass. | 4 to 5 ng/m ³ |
| Eisenreich | 2 | Various Dates to 1979 | Great Lakes, Various Locations | 0.4 to 3 ng/m ³ |
| Bidleman | 13 | 1973-1974 | Bermuda | 0.08 to 0.66 ng/m ³ |
| Bidleman | 13 | 1974? | Chesapeake Bay | 1 to 2 ng/m ³ |
| Bidleman | 13 | 1974? | Atlantic Ocean | 0.72 to 1.6 ng/m ³ |
| Andren | 13 | Mid 1970's? | Lake Michigan | 0.12 to 1.46 ng/m ³ |
| Ri | U.S. EPA | Aug 21-25 1979 | Lake Michigan | 3.3 ng/m ³ |
| Rice | U.S. EPA | Oct 1979 | Lake Superior | 0.15 ng/m ³ |
| Bidleman | 16 | 1973-1975 | Kingston, R.I. | 1 to 15 ng/m ³ |
| Eisenreich | 2 | 1979 | Minneapolis, Minnesota | 1.3 to 20 ng/m ³ |

MEASUREMENTS OF CONCENTRATIONS OF PCB IN LANDFILL GASES

| <u>RESEARCHER</u> | <u>REFERENCE</u> | <u>SAMPLE DATE</u> | <u>LANDFILL</u> | <u>PCB CONCENTRATION</u> |
|-------------------|---------------------|--------------------|-------------------------------|---------------------------|
| Murphy | 9 | 1976? | Chicago Landfill Gas | 3,240 ng/m ³ |
| N.Y. State | DeZolt (Priv. Com). | 1977? | Air Near Caputo PCB Dump Site | 300,000 ng/m ³ |

PCB concentrations expressed in nanograms per cubic meter of air.

TABLE 2
MEASUREMENTS OF DRY PCB DEPOSITION FROM ATMOSPHERE

| <u>RESEARCHER</u> | <u>REFERENCE</u> | <u>SAMPLE DATE</u> | <u>LOCATION</u> | <u>PCB DEPOSITION</u> |
|-------------------|------------------|--------------------|----------------------------------|------------------------------------|
| Rice | U.S. EPA | April 29, 1980 | Public Dock, Waukegan Harbor, IL | 1,208 ng/m ² /day |
| Bidleman | 16 | 1976-1979 | Columbia, S.C. | 35 to 392 ng/m ² /day |
| Bidleman | 16 | 1977-1979 | North Inlet, Estuary, S.C. | 3 to 74 ng/m ² /day |
| Bidleman | 16 | 1973-1975 | Kingston, R.I. | 298 to 421 ng/m ² /day |
| McClure | 30 | 1973 | La Jolla, California | 567 to 3840 ng/m ² /day |

MEASUREMENTS OF PCBs IN RAINFALL AND SNOWFALL

| <u>RESEARCHER</u> | <u>REFERENCE</u> | <u>SAMPLE DATE</u> | <u>LOCATION</u> | <u>PCB CONCENTRATION</u> |
|-------------------|------------------|--------------------|------------------------------------|--------------------------|
| Murphy | 9 | 1975-1976 | Chicago, IL (rain) | 160 ng/l (arith. avg) |
| Murphy | 9 | 1975-1976 | Chicago, IL (snow) | 212 ng/l (arith. avg) |
| Murphy | 9 | May-Oct 1976 | Beaver Island, Michigan (rain) | 215 ng/l (arith. avg) |
| Murphy | 9 | 1975-1976 | Chicago & Beaver Island | 111 ng/l (wt. avg) |
| Murphy | 13 | 1975-1976 | Lake Michigan (rain) | 119 ng/l (wt. avg) |
| Swain | 13 | 1978? | Duluth, Minn (snow) | 50 ng/l |
| Swain | 13 | 1978 | Isle Royale, Mich (snow) | 97.5 ng/l |
| Murphy | 13 | Late 1970's? | Saginaw Bay, Mich. (rain and snow) | 19 ng/l |

2.2 Solubility of PCBs in Water

2.2.1 Mason & Hanger Measurements

Mason & Hanger completed in August 1980 a series of bench scale treatment tests on contaminated Waukegan Harbor sediments. PCB-contaminated soils and sediments were slurried with Waukegan Harbor water (simulating dredging) which contained about one part per billion of PCB. The slurried soils or sediments were allowed to settle. A cationic polymer was then added to the turbid supernatant to coagulate the fines. The clarified material was then passed through a sand filter and a carbon filter. The effluent from the carbon filter contained less than one part per billion of PCB. However, the feedwater to the carbon filter still contained considerable PCBs indicating that PCBs solubilized in the water. Two test results are as follows:

| <u>PCBs in Sediment to be Slurried</u> | <u>PCBs in Sand Filter Water After Slurring and Settling</u> |
|--|--|
| 143 mg/kg (muck) | 79 ppb Aroclor 1242 |
| 3580 mg/kg (sand) | 132 ppb Aroclor 1242 |

The suspended solids in the filtered water were essentially zero. Raltech Scientific Services, Madison, Wisconsin, who performed the analytical work, reported that the filtered water con-

tained soluble PCB which most closely matched an Aroclor 1242 standard. The PCB contamination was not pure Aroclor 1242 as it contained some of the higher-chlorinated isomers suggestive of Aroclor 1254.

Mason & Hanger believes that when Wuakegan Harbor is dredged and the contaminated slurry is placed in the lagoon, some of the PCBs will solubilize. The lagoon water may contain on the order of 100 ppb of soluble PCB. This PCB can volatilize into the atmosphere. Only soluble PCB in water is available for volatilization.

The value for solubility of PCB in water can represent an upper limit of PCB available for volatilization.

2.2.2 Published Values for Solubility of PCBs in Water

Table 3 shows a wide variation in published PCB solubility values in water, even when comparing the same Aroclor at the same temperature.

Values ranging from 200 ppb to 703 ppb have been obtained for Aroclor 1242 under ambient conditions; there are a number of unpublished values outside this range, up to 2 (ppm) of Aroclor 1242 in water. Published Aroclor 1254 values under ambient conditions range from 12 ppb to 70 ppb. All researchers agree that Aroclor 1254 is less soluble in water than Aroclor 1242.

There are several reasons for the variations in published PCB solubility values:

1. Aroclor 1242 or 1254 is a mixture of PCB isomers, each with differing solubility values. If Aroclor 1242 is mixed with water, the lower-molecular weight isomers tend to solubilize in water. The soluble portion of PCB in water will therefore have a different isomeric distribution than the original Aroclor 1242 mixture. Therefore PCB analysis of the saturated water is difficult if compared with an Aroclor 1242 standard. A similar problem occurs with the other isomers. There also may be differences between batches of Aroclor 1242 or 1254.
2. Griffin (5) reported that up to 5 months may be required for the isomers of Aroclor 1242 to come to equilibrium when stirred with water. The equilibrium time for Aroclor 1252 is 2 months. Most researchers terminate their solubility test long before that time and therefore report low readings. Haque (15) agrees that this long a time may be required for the Aroclors to come to equilibrium, but the bulk of the solubilization is achieved very rapidly.
3. If too much agitation is applied during a solubility test with liquid PCB and water, a stable dispersion of submicron particles of PCB can form in water resulting in an artificially high PCB solubility in water.

4. Minerals in water can suppress the solubility of PCB (a salting out effect).
5. Organic materials in water may increase the solubility of PCB.
Benzene trichloride, a component of most capacitor fluids with PCB, increases the solubility of PCB. Humic acids in water also increases PCB solubility. For example, Wiese (22) found that the solubility of Aroclor 1254 in sea water was decreased 12 percent if the sea water was first passed through a carbon filter to remove trace organics before contacting with Aroclor 1254.

Table 4 shows that the isomer distribution of the water-soluble portion of a saturated solution of Aroclor 1242 or 1254 is very different compared with the virgin material. For example, only 3% by weight of Aroclor 1242 contains isomers of one chlorine atom, but the water soluble portion of PCB contains 19.4% isomers of one chlorine atom. This 19.4% is made up of 17.3% 2-chlorobiphenyl and 2.1% 4-chlorobiphenyl. Furthermore, the solubility of the individual isomers depend upon other isomers present. For example the isomer 2, 2'-bichlorobiphenyl is soluble to the extent of 21.18 ppb when present in Aroclor 1242 but is soluble to the extent of 900 ppb if the pure isomer is contacted with water. Different Aroclor 1242 batches can also vary in isomer content. The batch needs to be 42 ± 4 percent chlorinated to be classified as Aroclor 1242.

TABLE 3
SOLUBILITY OF PCB IN WATER

| <u>Aroclor</u> | <u>Solubility</u> | <u>Researcher</u> | <u>Remarks</u> |
|----------------|-------------------------------|-----------------------------------|--|
| 1242 | 703 $\mu\text{g}/1$ (23°C) | Griffin (5) | 5 mos. test |
| 1242 | 340 $\mu\text{g}/1$ (25°C) | Paris (referenced by Griffin) | |
| 1242 | 200 $\mu\text{g}/1$ (room) | Tucker (referenced by Griffin) | |
| 1242 | 240 $\mu\text{g}/1$ (25°C) | Mackay (10) | |
| 1242 | 200 $\mu\text{g}/1$ (20°C) | Nisket (referenced by Griffin) | |
| 1254 | 70 $\mu\text{g}/1$ (23°C) | Griffin (5) | 2 mos. test |
| 1254 | 45 $\mu\text{g}/1$ (room) | Lawrence (24) | |
| 1254 | 56 $\mu\text{g}/1$ (room) | Haque (15) | |
| 1254 | 12 $\mu\text{g}/1$ (25°C) | Mackay (10) | |
| 1254 | 50 $\mu\text{g}/1$ (20°C) | Nisket (referenced by Griffin) | |
| 1254 | 43 $\mu\text{g}/1$ (26°C) | Nelson (referenced by Griffin) | Membrane filtered Sea Water Carbon Filtered Sea Water |
| 1254 | 41 $\mu\text{g}/1$ (4°C) | Nelson (referenced by Griffin) | |
| 1254 | 28.1 $\mu\text{g}/1$ (16.5°C) | Wiese (23) | |
| 1254 | 24.7 $\mu\text{g}/1$ (16.5°C) | Wiese (23) | |

TABLE 4

MOLECULAR COMPOSITION OF AROCLOR 1242 AND AROCLOR 1254
AND THEIR WATER SOLUBLE ISOMERS
(DATA OF GRIFFIN (5))

| <u>Chlorobiphenyl</u> | <u>Virgin Aroclor</u> | | <u>Water Soluble Portion</u> | |
|-----------------------|-----------------------|---------------------|------------------------------|---------------------|
| | <u>Aroclor 1242</u> | <u>Aroclor 1254</u> | <u>Aroclor 1242</u> | <u>Aroclor 1254</u> |
| $C_{12}H_9Cl$ | 3% | - | 19.4% | - |
| $C_{12}H_8Cl_2$ | 13% | 2% | 32.2% | - |
| $C_{12}H_7Cl_3$ | 28% | 18% | 31.7% | 5.3% |
| $C_{12}H_6Cl_4$ | 30% | 40% | 15.8% | 37.0% |
| $C_{12}H_5Cl_5$ | 22% | 36% | 0.9% | 36.5% |
| $C_{12}H_4Cl_6$ | 4% | 4% | - | 21.2% |

COMPARISON OF AQUEOUS SOLUBILITY OF SOME
PCB ISOMERS CONTAINED IN AROCLOR 1242 TO THE
PURE INDIVIDUAL ISOMER (GRIFFIN (5))

| <u>Isomer</u> | <u>Solubility, ppb (23°C)</u> | |
|---------------------------------|--------------------------------|-----------------------------|
| | <u>In Aroclor 1242 Mixture</u> | <u>Pure Isomer In Water</u> |
| 4 - chlorobiphenyl | 15.07 | 400 |
| 2,2' - dichlorobiphenyl | 21.18 | 900 |
| 2,4' - dichlorobiphenyl | 138.93 | 637 |
| 2,5,2' - trichlorobiphenyl | 61.35 | 248 |
| 2,5,2',5' - tetrachlorobiphenyl | 22.25 | 26.5 |

REMARK: In this report, ppb (parts per billion) concentration is equivalent to $\mu g/l$ (micrograms per liter).

2.3 Adsorption/Desorption of PCBs on Soils and Sediments

A review of experimental work on adsorption and desorption of PCBs onto soils and sediments from aqueous solutions has been published by Griffin (5). The hydrophobic characteristic of PCBs make them readily adsorbed from aqueous solutions onto available surfaces. The degree of adsorption increases with surface area and organic content of the soil or sediment. Higher chlorinated PCB isomers are preferentially adsorbed by soil material and less likely to be desorbed than lower chlorinated isomers. There is some tendency for lower chlorinated isomers to be degraded by microorganisms.

Griffin (5) compared the adsorption tendency of water-soluble PCBs onto five earth materials. The materials, ranked in order of adsorption tendency were as follows:

| | |
|-----------------------------|------------------|
| medium temperature coal tar | ($K_F = 1938$) |
| high temperature coal tar | ($K_F = 1220$) |
| catlin soil | ($K_F = 532$) |
| montmorillonite clay | ($K_F = 172$) |
| Ottawa silica sand | ($K_F = 22$) |

Griffin determined the Freundlich adsorption constant K_F for each of these materials, defined by the following relationship:

$$\frac{X}{M} = K_F C$$

$\frac{X}{M}$ = amount of PCB adsorbed per unit weight of soil (mg/kg)

C = concentration of PCBs in the water at equilibrium (ppm)

N = empirical constant; experimentally = 1.0

The $K_F = 532$ value for catlin soil, for example, means that if the PCB concentration is 100 ppb (0.1 ppm) in solution at equilibrium, the concentration of PCB in the soil would be 53.2 mg/kg (ppm). Griffin (5) was further able to correlate K_F with the total organic carbon (TOC) content of the soil for $\text{TOC} > 2\%$.

$$K_F = 255 + 18.5 (\text{TOC})$$

TOC = percent total organic carbon

The Waukegan Harbor muck sediments appear to have a TOC value on the order of about 5 percent which corresponds to a K_F value of 350 using Griffin's equation. However, caution should be used because the Waukegan Harbor sediments have different surface areas than the soils that Griffin tested. Also, the organic content is at least in part biological rather than the coal tars which Griffin tested. Measurements of solubility of PCBs in water and of sediment PCB concentration (completed

by Mason & Hanger in August 1981) suggest K_F may be on the order of 2000 for Waukegan Harbor muck.

Table 5 presents values of K_F for various materials. High values of K_F for various materials indicate that the material readily adsorbs PCBs. Activated sludge has a value on the order of 20,000 to 70,000 compared with 10 or 20 for sand and soils with low organic content. Goodrich 1115 foam, a dispersion resin used for insulation, has a value of $K_F = 200,000$. These values are considerably higher than Griffin's limiting value of $K_F = 255 + 18.5 (100) = 2105$ for 100 percent TOC. Materials with a high K_F value can potentially remove large quantities of PCB if slurred with water contaminated with PCB.

Griffin (5) reported that PCBs adsorbed onto soils remained immobile when leached with water especially if the material had a high K_F value. Higher chlorinated isomers were more immobile than lower chlorinated isomers. The PCBs could be readily leached from the soils with organic solvents such as carbon tetrachloride, benzene, acetone and methanol. The PCB contaminated soils or sediments stored in the same landfill location where organic solvents are present can potentially leach PCBs.

TABLE 5
FREUNDLICH ADSORPTION CONSTANTS FOR PCBs ON SELECTED MATERIALS
AROCOR 1242 EXCEPT WHERE INDICATED

$$\frac{X}{M} = K_F C^N$$

$\frac{X}{M}$ = mg of PCB per kg of Material

C = ppm of PCB in water at equilibrium

| <u>Researcher</u> | <u>Reference</u> | <u>Material</u> | <u>K_F</u> | <u>N</u> |
|-------------------|------------------|---------------------------------|----------------------|----------|
| Griffin | (5) | medium temp coal tar | 1938 | 1.0 |
| Griffin | (5) | high temp coal tar | 1220 | 1.0 |
| Griffin | (5) | Ottawa sand | 22 | 1.0 |
| Hiraizumi | (11) | plankton (ocean) | 10,000 | 1.0 |
| Aizawa | (11) | activated sludge | 20,000 to 70,000 | 0.6 |
| Hague | (15) | woodburn soil (Aroclor 1254) | 10 | 1.1 |
| Griffin | (5) | montmorillonite clay | 172 | 1.0 |
| Lawrence | (24) | Amberlite XAD-4 | 20,000 | variable |
| Lawrence | (24) | Goodrich 1115 foam | 200,000 | variable |
| Calgon Corp. | Personal Comm. | Carbon (Aroclor 1221) | 242 | 1.43 |
| Calgon Corp. | Personal Comm. | Carbon (Aroclor 1232) | 630 | 1.37 |

2.4 Volatilization of PCBs From Water

The volatilization of a chemical dissolved in water is a first-order kinetic process, expressed as follows (steady state):

$$N_1 = kv (C_1 - P_1/H_1)$$

Where N_1 = volatilization rate (e.g. pounds per hour per square foot or other dimensionally-consistent units)

kv = volatilization rate constant

C_1 = concentration of chemical in the liquid

P_1 = partial pressure of the chemical in the air

H_1 = Henry's Law Constant

If $C_1 > P_1/H_1$, then the chemical will volatilize into the atmosphere; otherwise the water concentration of the chemical will tend to increase until $C_1 = P_1/H_1$.

General Electric (1) has reported a Henry's Law Constants of $H = 9.06 \times 10^{-5} \text{ atm m}^3/\text{mole}$ for Aroclor 1242 and $H = 4.76 \times 10^{-5} \text{ atm m}^3/\text{mole}$ for Aroclor 1254 under ambient conditions. They obtained these values of H using a laboratory test cell containing 50 ppb of PCB in deionized water.

If the concentration of PCB in the atmosphere near Lake Michigan is assumed to be one nanogram per cubic meter, the partial pressure will be:

$$\frac{10^{-9}}{261} \times \frac{29}{1184} = 9.4 \times 10^{-14}$$

Using $H = 9.06 \times 10^{-5} \text{ atm} \cdot \text{m}^3/\text{mole}$, the equilibrium concentration in water would be $C = (9.4 \times 10^{-14}) / (9.09 \times 10^{-5}) = 1.03 \times 10^{-9} \text{ moles per cubic meter}$ or $1.03 \times 10^{-9} (261) = 2.7 \times 10^{-7} \text{ grams/m}^3$ or $2.7 \times 10^{-4} \text{ ppb}$. The average molecular weight of Aroclor 1242 is 261.

The concentration of PCB expected in the lagoon water at Waukegan Harbor should be on the order of 10 to 100 ppb. Since this number is much larger than $2.7 \times 10^{-4} \text{ ppb}$, there should be net volatilization of PCBs to the air.

The Henrys Law Constant is, however, difficult to measure. Published values vary. For example, Mackay (10) reports an equilibrium value of $4.06 \times 10^{-4} \text{ mm HG}$ of PCB in the air in contact with a saturated solution of 240 ppb of Aroclor 1242. This corresponds to a Henry's Law Constant of,

$$H_1 = \frac{P_1}{C_1} = \frac{261}{240} \left(\frac{4.06 \times 10^{-4}}{760} \right) = 5.8 \times 10^{-7} \text{ atm} \cdot \text{m}^3/\text{mole}$$

Eisenreich (2) lists several H_1 values for Aroclor 1242 varying from 1×10^{-7} to $5.6 \times 10^{-4} \text{ atm/m}^3 \text{ mole}$. If $H_1 = 1 \times 10^{-7} \text{ atm/m}^2 \cdot \text{mole}$ and $P_1 = 9.4 \times 10^{-14} \text{ atm}$, then the equilibrium concentration of

C_i would be 0.25 ppb. This number is still much smaller than the expected PCB concentration in the lagoon at Waukegan Harbor so there should be a net volatilization of PCBs into the air.

Even using $H_i = 10^{-7}$ atm - m³/mole, the value of P_i/H_i is expected to be much less than the value of C_i, the concentration of PCBs in the water contained in the Waukegan Harbor lagoon. For all practical purposes, the P_i/H_i term can be dropped and the volatilization rate of PCB be assumed proportional to the concentration of PCB in the lagoon water.

$$N_i = k_v C_i$$

$$C_i > 2 \text{ ppb}$$

There is much discussion in the literature as to whether the liquid film or the gas phase mass transfer coefficient controls k_v . Mackay (13) reports if H_i is greater than 5×10^{-3} atm - m³/mole, resistance to mass transfer is in the liquid phase and if H_i is less than 5×10^{-6} atm - m³/mole, resistance to mass transfer is in the gas phase. The published literature values of H_i span this entire range. Doskey and Andren (32) report values of H_i in the range of 10^{-6} and 10^{-7} atm - m³/mole which would correspond to the gas phase controlling resistance. Tofflemire (1) and Murphy (9) state in their papers that the liquid phase controls resistance. Tofflemire (1) further compares PCB volatilization with oxygen transfer in water in order to extract certain relationships (for example, k_v is assumed equal to the liquid phase mass transfer coefficient, and that this coefficient is propor-

tional to $1.025^{(T-20)}$ where T is the temperature in degrees Centigrade). This relationship was found experimentally to hold for oxygen and is assumed by Tofflemire to hold true for PCB.

General Electric found experimentally that the wind velocity strongly affects volatilization rate of PCB from water. Tofflemire (1) says the wind results in waves which disturb the water and increase the liquid-controlling mass transfer coefficient. Stirring of laboratory test tanks also increases PCB volatilization rate from water.

The volatilization rate constant, k_v , is made up of a liquid rate mass transfer coefficient, K_L and a gaseous rate mass transfer coefficient, K_g .

$$\frac{1}{k_v} = \frac{1}{K_L} + \frac{RT}{HK_g}$$

Whether the gas or liquid phase transfer coefficient is controlling, the volatilization rate of PCB is still proportional to the concentration of PCB in the water (as long as the concentration of PCB in the water is more than a few ppb and the partial pressure in the air is low).

$$N_i = K_L C_i$$

liquid phase controls

$$N_i = \frac{RT}{HK_g} C_i$$

gas phase controls

Tofflemire (1), who states that the liquid film transfer resistance controls, introduces a "tank depth" or "river depth" into his calculations for estimation of PCB volatilization rate:

$$N_i = K_L C_i$$

$$K_L = k_{PCB} d$$

d = tank depth (units of feet, meters, etc)

k_{PCB} = volumetric transfer coefficient (units of hr^{-1})

This line of reasoning would result in a 10 foot deep tank or lagoon having ten times the volatilization rate as a one foot depth lagoon. The volatilization rate from certain portions of the ocean where the depth exceeds 30,000 feet would be excessive.

Mason & Hanger suggests instead that K_L is really the PCB diffusion coefficient divided by the liquid film thickness y . The liquid film thickness y is of the order of a millimeter thickness or less and is a function of the degree of turbulence in the water. Then,

$$N_i = \frac{D_i (C_i - C_o)}{y} \approx \frac{D_i C_i}{y}$$

Where C_i = conc. of PCB in the liquid

C_o = conc. of PCB at the air-water interface (assume much smaller than C_i)

Smith, James H., et al (33) of SRI International has published a more thorough discussion on volatilization rate mass transfer coefficients.

Blanchart (25) claims that bubble formation in lakes and other bodies of water may result in significant volatilization and transfer of pollutants to the atmosphere.

Tofflemire (1) published General Electric measurements of PCB volatilization rates from tap water saturated with Aroclor 1242. General Electric used a test tank 31 inches high and 8 inches in diameter. The test tank was fitted with a sealed header over the top. Air flow, measured by a variable area air flow meter, was introduced into the header. The outgoing air was passed through a PCB sampling device containing three polyurethane sponges which adsorbed the PCB. After the test, the sponges were removed and washed with nanograde hexane. A gas chromatograph with a silver halide detector was used to measure PCB. The water in the tank was stirred with a 6.75 in. by 1.5 in. paddle blade at 60 to 80 rpm during the tests.

The General Electric data for the test tank are presented in the Appendix. According to Charles McFarland of General Electric, PCB liquid was pipetted into the test tank. The test tank water was stirred overnight at 10°C.

Then PCB measurements in the air were taken at 10°C at the three air speeds, each measurement taking about a day. The tank was then heated to 20°C and measurements were taken at that temperature. After the last measurement was taken at 50°C (21 mg/m²/hr PCB loss for 0.87 m/sec air speed and 50°C), the tank was then opened. PCB liquid was still seen at the bottom of the tank so the assumption was made that PCB was saturated in water at all temperatures measured. Direct measurements of PCB concentration in the water were not taken. The saturation value of Aroclor 1242 at 20°C or any temperature is subject to debate because different values have been obtained by different researchers depending upon how the measurement was made.

The water surface area of the proposed South Lagoon at Waukegan Harbor when full will be about 280,000 square feet (26,000 square meters). If the assumption is made that the water temperature is 15°C, General Electric data predict a PCB volatilization rate of 3.8 mg/m²/hr at 1.62 meters/second air speed.

The solubility of PCB in water at 15°C is probably on the order of 200 ppb (Table 3). If the concentration of PCB in the lagoon is 100 ppb, 0.1 lbs/hr of PCB would be volatilized from the lagoon, according to the following calculation:

$$\frac{3.8 \text{ mg}}{\text{m}^2 \text{ hr}} \left(\frac{100}{200} \right) \left(\frac{26,000 \text{ m}^2}{453,600 \text{ mg}} \right) \text{ lb} = 0.109 \text{ lbs/hr}$$

A different prediction of volatilization rate is obtained using Tofflemire's (1) value for the liquid transfer film coefficient which incorporates the tank depth in the calculation. At 1.62 m/sec air speed and 20°C, $k_{\text{PCB}} = 0.0267 \text{ hr}^{-1}$ as published in Tofflemire's paper. Correcting to 15°C,

$$0.0267 (1.025)^{15-20} = 0.0236 \text{ hr}^{-1}$$

For a lagoon depth of 15 feet, lagoon area 280,000 square feet, lagoon concentration of 100 ppb, the following volatilization rate is calculated:

$$N_1 = k_{\text{PCB}} d C_1$$

$$N_1 = \frac{0.0236}{\text{hr}} (15 \text{ ft}) \frac{(10)^{-7} \text{ lbs } 62.3 \text{ lbs water}}{\text{lbs water } \text{ft}^3}$$

$$N_1 = 2.2 \times 10^{-6} \text{ lbs/hr} - \text{ft}^2$$

$$\text{PCB volatilization} = 2.2 \times 10^{-6} (280,000) = 0.62 \text{ lbs/hr}$$

Mason & Hanger is of the opinion that the use of the depth in this way results in an erroneous answer. If Tofflemire's uncorrelated value of $k_L = 0.78 (0.0267) = 0.0208 \text{ meters/hr}$ is used (The G. E. test tank depth was 0.78

meters), the same calculation predicts a total PCB volatilization rate of about 0.10 lbs/hr from the lagoon. Mason & Hanger believes that the tank depth should not enter into the calculation and the data should be scaled directly.

Very few measurements of PCB, volatilization from water has been published other than the work of General Electric as discussed by Tofflemire.

Griffin (5) measured the rate of PCB volatilization from pure water containing humic acid, and water containing Catlin soil. The test apparatus was a simple 1000 mg Erlenmeyer flask containing 100 ml of PCB solution at 25°C. The flask contents were stirred using a magnetic stirrer. The flask was purged with nitrogen at 200 ml/min, the purged nitrogen passed through a hexane trap to remove PCBs. The hexane was injected into a gas-chromatograph column filled with a flame ionization detector for PCB analysis. Griffin reported his results on the basis of a percentage PCB volatilized from the test flask rather than as a volatilization rate.

| <u>Conditions</u> | <u>Percent Aroclor 1242 Volatilized From Flask in 20 Minutes</u> |
|--|--|
| 50 ppb PCB in water | 3.5 percent |
| 50 ppb PCB in 500 ppm Humic Acid Solution | 3.6 percent |
| 50 ppb PCB, 6400 ppm Catlin Soil, Water | 0.74 percent |

The effect of the humic acid and the soil was to reduce the volatilization of PCB from water.

Unfortunately, Griffin's data cannot be used directly to predict the PCB volatilization rate from the proposed Waukegan Harbor lagoons.

2.5 Volatilization of PCB's and Other Chlorinated Hydrocarbons from Soils and Methods of Control

Published measurements of volatilization of PCB from contaminated soils is limited; most measurements have been done by the New York Department of Environmental Conservation or General Electric in conjunction with PCB dump sites or the Hudson River PCB spill in New York State. On the other hand, a fair amount of information has been published by several researchers (notably, W. Spencer, V. H. Freed, R. Hague, R. A. Leonard, W. J. Farmer, M. M. Cliath, W. D. Guenzi, W. E. Beard, J.P. Martin, T. F. Bidleman and others) on volatilization of pesticides and pesticide residues from soils. Walter J. Farmer, et al under US EPA (Cincinnati, Ohio) contract published information on hexachlorobenzene volatilization from soils in dump sites.

Tofflemire has kindly supplied Mason & Hanger with a summary of data taken by the New York Department of Environmental Conservation (DEC) and by General Electric. The data are presented in the Appendix of this report. Volatilization rates and measurements of PCB concen-

centrations in the air are reported as Aroclor 1242 or 1012. The sediments tested were of a sandy nature so PCB volatilization rates would be expected to be higher (for a given sediment concentration of PCB) than Waukegan Harbor muck.

The New York DEC developed an empirical correlation relating concentration of PCB in the air to concentration of PCB in the sandy sediment under ambient conditions and low wind speed:

$$y = 0.0135 - 0.0023 x$$

y = ratio of Air PCB conc. to Sediment PCB conc.

x = \log_{10} of the sediment PCB conc. in ppm, $1 < x < 5$

General Electric measured $0.7 \mu\text{g}/\text{m}^3$ PCB in the air in contact with Bouy 212 sandy sediment containing 64 ppm PCB at a speed of 0.73 mph. The empirical correlation predicts the following:

$$y = 0.0135 - 0.0023 \log_{10} 64$$

$$y = 0.00935$$

$$\text{Predicted air concentration} = 0.00935 (64) = 0.60 \mu\text{g}/\text{m}^3$$

$$\text{Measured air concentration} = 0.7 \mu\text{g}/\text{m}^3$$

An approximate correlation between concentration of PCB in the air, wind speed, and volatilization rate appears to hold true for the GE tank data. At a wind speed of 0.73 mph, a volatilization rate of 114 $\mu\text{g}/\text{m}^2/\text{hr}$ was measured and the concentration of PCB in the air was 0.7 $\mu\text{g}/\text{m}^3$ when Buoy 212 sediment was studied. For other situations, the volatilization rate appears to be proportional to the wind speed and PCB concentration in the air. For example:

- a. Predicted volatilization from 3A Remnant sandy soil

$$114 \left(\frac{3.6}{0.73} \right) \left(\frac{3.5}{0.7} \right) = 2811 \mu\text{g}/\text{m}^2/\text{hr}$$

Measured volatilization from 3A Remnant was 2672 $\mu\text{g}/\text{m}^2/\text{hr}$

- b. Predicted volatilization from Caputo sandy soil

$$114 \left(\frac{3.6}{0.73} \right) \left(\frac{70}{0.7} \right) = 56219 \mu\text{g}/\text{m}^2/\text{hr}$$

Measured volatilization from Caputo sandy soil was 47,770 $\mu\text{g}/\text{m}^2/\text{hr}$

- c. Predicted air concentration of PCB near Caputo sandy soil

$$y = 0.0135 - 0.0023 \log_{10} (20,000)$$

$$y = 0.0036$$

$$0.0036 (20,000) = 72 \text{ } \mu\text{g}/\text{m}^3$$

Measured PCB concentration in air near Caputo sandy soil was

$$70 \text{ } \mu\text{g}/\text{m}^3$$

The actual amount of PCB volatilized from exposed Waukegan Harbor sediments should be less because (1) the volatilization rate from Waukegan Harbor muck should be less than from sand and (2) PCB left in exposed sediments would become depleted so the volatilization rate should decrease with time. The PCB-depleted sediments should form a cap on deeper sediments decreasing volatilization.

From the New York data, a table can be constructed predicting volatilization rates from sandy sediment placed in the proposed Waukegan Harbor lagoons. For convenience, it is assumed that the exposed sediment (the dikes of the lagoon plus settled sediment after draining and treating excess water) area totals 280,000 square feet. The wind speed is assumed to be 3.6 mph and the air temperature is 20°C (68°F).

Predicted Volatilization Rates From Sandy Sediment
In Proposed Waukegan Harbor Lagoon

| PCB Conc in Exposed Sediment PPM | Predicted PCB Conc. in Air | Volatilization Rate $\mu\text{g}/\text{m}^2/\text{hr}$ | Total Lbs PCB Volatilized from Exposed Sediment in 60 Days |
|--|-------------------------------|---|---|
| 10 | 0.112 | 90 | 7.4 |
| 100 | 0.89 | 725 | 60 |
| 1000 | 6.6 | 5375 | 444 |
| 10000 | 43 | 35000 | 2900 |
| 100000 | 200 | 163000 | 13500 |

The actual amount of PCB volatilized from exposed Waukegan Harbor sediments should be less because (1) the volatilization rate from Waukegan Harbor muck should be less than that from sand and (2) PCBs left in exposed sediments would become depleted so the volatilization rate should decrease with time. The PCB depleted sediments should form a cap on deeper sediments decreasing volatilization.

Tofflemire (1) has estimated that the half life of PCB in the top 10 cm of Bouy 212 sand originally containing 64 ppm PCB is 0.1 year at 20°C. This means that after about 0.1 year, the average concentration in the sand would have decreased from 64 ppm to 32 ppm because of volatilization. This compares with a half-life of Aroclor 1242 of only 6 hours from a one meter column of water, estimated by Mackay (10). Estimates of half life of PCB in soils or water columns volatilizing to the air are summarized below:

| <u>Researcher</u> | <u>Aroclor</u> | <u>Soil</u> | <u>Half Life</u> |
|----------------------|----------------|--------------------------|------------------|
| Mackay (10) | 1242 | one meter of water | 6 hours |
| Mackay (10) | 1248 | one meter of water | 1 hour |
| Mackay (10) | 1254 | one meter of water | 1.2 minutes |
| McClure (30) | 1254 | 10 cm LaJolla, Ca., Soil | 6 years |
| General Electric (1) | 1016 | 10 cm Bouy 212 sand | 0.1 year |
| Hague (15) | 1254 | 10 cm Ottawa sand | 0.1 year |
| General Electric (1) | 1242, 1254 | 10 cm top soil | over 0.3 years |

The available data seem to indicate that PCBs are more readily volatilized or depleted from water columns than from sand or soils. The

PCBs are more readily volatilized or depleted from sandy soils than from finely-divided silts or soils with a high organic content. The higher-chlorinated Aroclors are more readily volatilized from water but are less readily volatilized (e.g. more tightly bound to) from soils.

Some additional conclusions may be learned from volatilization of pesticides from soils which appear to be applicable towards volatilization of PCBs. Some general conclusions are listed below:

1. Like PCBs, pesticide volatilization is the major mechanism by which pesticides such as lindane, DDT, etc. are dispersed throughout the atmosphere. Pesticide volatilization is related to vapor pressure of the chemical. Unlike PCBs, pesticide can degrade to other products while still in the soil and these degregation products can volatilize (have higher vapor pressure) more readily than the parent compound.
2. Volatilization rate of pesticides is much more rapid from soils immediately after disking (fresh contaminated soil is exposed to the air).
3. Diffusion of pesticides from deeper soils to the surface is the rate controlling step in volatilization as the surface soil lose their original pesticide content from volatilization.

4. Volatilization of at least some kinds of pesticides is greater from wet soils than from dry soils.
5. Pesticides can co-distill with water (both water and the pesticide vaporize from the surface) when, the sediments or soils are warm. Co-distillation is not important under lower temperatures.
6. If the pesticide is not readily adsorbed on the soil surface, the vapor pressure of the pesticide and the diffusion of the pesticide from deeper soil layers to the surface are the rate controlling steps in volatilization.
7. Pesticides are less readily volatilized from soils containing a significant organic fraction or clay fraction as opposed to sand. Organic cationic pesticides are readily adsorbed onto clay.
8. Volatilization rate of pesticide from soils increased with concentration of pesticide in the soil. Eventually a saturation vapor density is reached equal to that of the pesticide without the soil.
9. Relative humidity indirectly affects pesticide volatilization rate. Low humidity will dry out (remove water)

the soils more rapidly. Once the soil is dry, volatilization of PCB decreases significantly. In addition, pesticide volatilization rate may increase if initially dry contaminated soil is exposed to a humid environment.

Walter Farmer (6) studied hexachlorobenzene volatilization from soils in landfills. He made the following conclusions:

1. Diffusion of vapor hexachlorobenzene through soil covers is the rate controlling step for dispersal of this chemical from landfills.
2. Covering of contaminated soils with non-contaminated soils or with water is an effective way of controlling hexachlorobenzene volatilization. Highly-compacted, wet soil covers are the most effective. Air-filled (porous) soil covers are the less effective because the chemical can volatilize into the air spaces and diffuse to the soil cover surface.
3. Polyethylene film is relatively ineffective in controlling volatilization. The hexachlorobenzene can diffuse right through the plastic film.
4. The solubility of hexachlorobenzene in water is low (6.2 ppb). The hexachlorobenzene does not readily solubilize in water from the soils. This makes water a good cover.

5. Each 10°C rise in soil temperature increases the HCB volatilization flux about 3.5 times.

Drs. A. T. McCord and R. C. Zeigler while employed by Calspan Corp., recently began a study of rates of emission of gases leaving industrial solid waste landfills. The study was never completed nor results published because of lack of funding. McCord (personnel communication) reported that benzene trichloride increases the solubility of PCB in water. He also confirmed that PCB can diffuse through plastic films. He mentioned a study being performed at the Los Alamos Scientific Laboratories that showed PCB especially in solvents such as benzene trichloride can diffuse through plastic gloves fabricated of various materials (rubber, polyethylene, etc). Mason & Hanger was unable to obtain a copy of the Los Alamos report.

3.0 APPLICATION TO WAUKEGAN HARBOR DREDGING OPERATIONS

3.1 Description of Waukegan Harbor Dredging Operations

The proposed Waukegan Harbor dredging plan calls for removal of 166,000 cubic yards of muck sediments over 10 ppm of PCB and placing the material in one or two lagoons to be constructed on a vacant land site adjacent to the Harbor. In addition, about 3,000 or 4,000 cubic yards of contaminated sand and clay will be removed from Slip #3 of the harbor and also placed in one of the lagoons. The excess lagoon water will be treated (sedimentation, filtration, carbon adsorption) such that when returned to the harbor the water will contain less than 1 ppb of PCB.

From Table 2 of the Mason & Hanger report submitted to the US EPA in January 1981, quantities and concentrations of contaminated muck are listed below:

| <u>Location</u> | <u>Avg. Concentration, PPM of PCB</u> | <u>Cubic Yards of Muck</u> |
|-----------------|---------------------------------------|----------------------------|
| A1 | 54,960 | 1,261 |
| A2 | 54,796 | 789 |
| A3 | 11,796 | 508 |
| A4 | 2,028 | 553 |
| A5 | 773 | 1,125 |
| A6 | 341 | 2,939 |
| B1 thru B5 | 136 | 37,574 |
| C1 thru C6 | 17 | <u>120,451</u> |
| Total A, B, C | | 165,300 |

A map is presented in the appendix showing these locations.

The most contaminated area (A1 thru A6) is in Slip #3 of Waukegan Harbor. Areas A1 and A2 with an arithmetic average concentration of about 55,000 ppm PCB (isolated pockets as high as 500,000 ppm PCB) is at the outfall (now sealed off) where PCBs were originally discharged. About 3,000 or 4,000 cubic yards of contaminated sand and clay exist beneath the top muck layer and on shore at the outfall location containing isolated pockets as high as 130,000 ppm PCB. Raltech Scientific Services, Inc. of Madison, Wisconsin, who did much of the analytical work, reported that the PCBs in the sediments matched most closely Aroclor 1242.

Mason & Hanger slurried Waukegan Harbor muck sediments and contaminated sand (obtained from nearby North Ditch) with water simulating dredging operations transferring contaminated material to the proposed lagoon(s). The slurried sediments were allowed to settle, assisted with a cationic polymer. The turbid supernatant was then filtered to remove suspended solids. The filtered water was then measured for soluble PCB.

| <u>Sediment Material</u> | <u>Sediment PCB Concentration</u> | <u>Soluble PCB in Water</u> |
|--------------------------|-----------------------------------|-----------------------------|
| Muck (Area A5) | 142 ppm | 71 ppb |
| Sand | 28,330 ppm | 132 ppb |

The solubility of Aroclor 1242 in water is at room temperature on the order of 200 or 300 ppb; as discussed earlier, the rate in which PCBs solubilize in water is very slow.

Nevertheless, when Slip #3 contaminated muck sediments is slurried into one of the lagoons, the water could contain on the order of 100 ppb of soluble PCB. The muck sediments would settle to the bottom of the lagoon leaving 100 ppb of PCB contained in the water. The concentration of soluble PCB would be expected to decrease as less contaminated sediments are placed in the lagoon. The more contaminated water would be drawn off and treated and replaced with less contaminated sediments and water. The less contaminated sediments should adsorb some of the PCBs in the water. Some of the soluble PCB will be lost from the surface because of volatilization. When the dredging is completed and excess water treated and discharged, the water remaining in the lagoon should be on the order of several parts per billion.

The concentration of soluble PCB in Waukegan Harbor (EPA funded studies) is reported to be on the order of 1 ppb or less; concentration in Slip #3 may at times exceed 1 ppb of PCB.

A possible projected scheduling for these operations is as follows:

Step 1: Dredge 7300 cubic yards of Slip #3 sediments over a period of 6 days. The lagoon could contain an estimated 78,000 cubic yards of water plus sediments after this dredging.

Step 2: During this time, no additional sediments are dredged. The water treatment plant is tested to insure that 1 ppb of water can be produced. This period of time is unknown, but for sake of discussion, a five day period is assumed.

Step 3: The 38,000 cubic yards of sediment in areas B1 thru B5 are dredged and placed in the lagoon. The water treatment system exports excess water back to the Harbor while dredging takes place. This period of time is expected to be about 40 days based on treating 1500 gpm of water and a slurry volume (sediment plus water) of 315,000 cubic yards.

Step 4: The 121,000 cubic yards of muck sediments in areas C6 are dredged. The sediments may be placed in a second lagoon. Alternatively, the first lagoon (containing muck sediments from area A1 thru A6 and B1 thru B5) is drained and its contents excavated to a landfill and then reused for sediments from areas C1 thru C6. Several months may elapse between Steps 4 and 5. Assuming that 900,000 cubic yards of slurry (water plus sediments) is transferred to the lagoon, and the water treatment system returns 1500 gpm to the Harbor, the total time for these operations could be 95 days (allowing for several days to check out the water treatment system).

Step 5: The dewatered (excess water removed and treated) sediment is excavated from the lagoon to a landfill.

The 3,000 or 4,000 cubic yards of contaminated sand and clay could either be hauled directly away to a landfill or placed in the lagoon (possibly after Step 3) for temporary storage.

3.2 Estimation of PCB Volatilization During Waukegan Harbor Dredging

Not enough information is known to estimate quantities of PCBs volatilized either in the Harbor or from the lagoons, or from final excavation of sediments to a landfill. Some assumptions must be made even after careful review of the literature on volatilization (discussed in Section 2). Each dredging operation should be considered separately.

3.2.1 Background

The water area location A1 thru A6, B1 thru B5 and C1 thru C6 of Waukegan Harbor is 1,190,000 square feet. The average PCB concentration is assumed to be 1 ppb. The data obtained in the General Electric test tank are assumed to apply; at 15°C and 1.62 m/sec air speed the Aroclor 1242 volatilization rate from a saturated solution (assumed to be 200 ppb) was $3.8 \text{ mg/m}^2/\text{hr}$. The volatilization rate is assumed to be proportional to the concentration of PCB in the water. Therefore, over a month's time, the following volatilization rate is predicted:

$$\frac{1}{200} \frac{3.8 \text{ mg}}{\text{m}^2 \text{ hr}} \frac{0.0929 \text{ m}^2}{\text{ft}^2} 1,190,000 \text{ ft}^2 \frac{1 \text{ lb}}{453,600 \text{ mg}} \frac{24(30) \text{ hr}}{\text{month}}$$

= 3.33 lbs per month

This volatilization rate compares with PCB atmospheric deposition to Lake Michigan of 0.7 lbs per square mile per year (Section 2.1.5). This calculates out to 0.0025 lbs per month deposition to Waukegan Harbor.

The volatilization rate of 3.33 lbs per month would, of course be much less during the winter and spring months when the water temperature is cold.

3.2.2 Step 1: Slip #3 muck sediments (7,300 cubic yards) are dredged over a period of 6 days and placed in a lagoon. The lagoon water is assumed to contain 100 ppb of soluble PCB. The lagoon water is assumed to be mixed with fresh dredged material which releases PCB to the water to replace PCBs lost by volatilization. When finished, the lagoon is assumed to contain 7,300 cubic yards of muck sediments and 71,000 cubic yards of water. The lagoon is not full of water at this stage so the average water surface area exposed to the air is assumed to be 210,000 square

feet. The General Electric test tank volatilization (saturated water, 15°C, 1.62 m/sec air speed) is $3.8 \text{ mg/m}^2/\text{hr}$. The following PCB volatilization is calculated for the 6 day period:

$$3.8 \left(\frac{100}{200} \right) (0.0929) \left(\frac{210,000}{453,600} \right) (24) (6) = 11.7 \text{ lbs of PCB}$$

3.2.3 Step 2: When dredging of Slip #3 is complete, the lagoon should contain 71,000 cubic yards of water containing 100 ppb of PCB. This calculates out to $0.1 (71,000) (27) (62.3) (10)^{-6} = 11.9$ lbs of PCB dissolved in this amount of water. Probably, the PCBs will be volatilized faster than the rate at which PCBs would be replaced by desorption from the muck sediments that have settled out of the lagoon. If this is true, the concentration of soluble PCB should begin to decrease. Mackay has estimated that the half life of Aroclor 1242 in a well-mixed column of water one meter deep is 6 hours under ambient conditions. The lagoon contains 3 meters of water corresponding to a half life of 18 hours. The actual half life of PCB in the lagoon would be expected to be greater than 18

hours because the water is not strongly agitated and the temperature may be lower. In addition, the water treatment system will take out contaminated water from the lagoon and return water of around 1 ppb to the lagoon during testing. Probably, several pounds (say about 5 lbs) of PCB may be volatilized during this estimated 5 day period.

3.2.4 Step 3: The 38,000 cubic yards of sediment from areas B1 thru B5 (sediment over 50 ppm and under 500 ppm PCB) are dredged and placed in the lagoon. The concentration of PCB in the water may vary anywhere from 1 ppb to possibly 100 ppb. If the PCB concentration is assumed to be 30 ppb and the surface area of the water is assumed to be 280,000 square feet, the following amount of PCBs could be volatilized over a 40 day period:

$$3.8 \left(\frac{30}{200} \right) (0.0929) \left(\frac{280,000}{453,600} \right) (24) (40) = 31 \text{ lbs.}$$

3.2.5 Draining the Lagoon and Excavating

The lagoon water is removed, treated, and discharged to the harbor. The sediments are then excavated. Based on General Electric

data developed for sand (Section 2.5), the following amounts of PCB is predicted to be volatilized:

| Conc. of PCB in Exposed Sediment PPM | Volatilization Rate ug/m ² /hr | Total lbs PCB Volatilization From Exposed Sediment in One Month |
|--|--|--|
| 1 | 10* | 0.4* |
| 10 | 90 | 3.7 |
| 100 | 725 | 30 |
| 1000 | 5375 | 222 |
| 10000 | 35000 | 1450 |
| 1000000 | 163000 | 6750 |

*Estimates for 1 ppb extrapolated.

As discussed in Section 2.5, the actual amount of PCB volatilized should be less because (1) volatilization should be less from finely-divided silt than sand and (2) the exposed sediments should form an inert cap preventing volatilization from deeper sediments as time progresses.

The sediment may have a water cap on it before excavation. The concentration of PCB in this water cap is unknown, but the low PCB half life and the slow solubilization of PCB from underlying sediments suggests that the concentration should be low, perhaps a few ppb of PCB or less.

If the concentration is 10 ppb and the area exposed is say 200,000 square feet:

$$3.8 \left(\frac{10}{200} \right) (0.0929) \left(\frac{200,000}{453,600} \right) (24) (30) = 5.6 \text{ lbs per month}$$

If the concentration is 1 ppb PCB in the water, the PCB volatilization rate would be 0.56 lbs per month.

3.2.6 Step 4: The 121,000 cubic yards of muck sediments in areas C1 thru C6 is dredged and placed in either an excavated first lagoon or in a second lagoon. These sediments contain an arithmetic average of 17 ppm and a maximum of about 50 ppm. The concentration of PCB in the water is unknown but should be much less than 100 ppb, perhaps on the order of only a few parts per billion. For example, if the concentration is 10 ppb of PCB, 280,000 square foot of area exposed, dredging time 95 days:

$$3.8 \left(\frac{10}{200} \right) (0.0929) \left(\frac{280,000}{453,600} \right) (24) (95) = 24.8 \text{ lbs.}$$

3.2.7 Step 5: The lagoon is drained and excavated. The amount of PCBs volatilized depends upon the concentration of PCBs in the exposed sediments and area of exposed sediments. When it is necessary to excavate the more contaminated sediments, the area exposed should be as small as possible. For example, calculations presented

earlier showed that 1,450 lbs/ month (48.3 lbs/day) of PCB should be volatilized from sandy sediment containing 10,000 ppm of PCB covering an area of 280,000 square feet. If this material were capped with uncontaminated material and later excavated exposing say only 200 square feet at a time, the volatilization rate would be only $48.3 \times \left(\frac{200}{280,000}\right) = 0.0343$ lbs/day. Also, if excavation were done during cool weather (October, November, March, April or May) volatilization should be less.

3.3 Controlling Volatilization

3.3.1 Isolate Highly-Contaminated Sediment

Almost all of the Waukegan Harbor sediment contains less than 500 ppm PCB. Most contains less than 50 ppm PCB. Roughly 2500 cubic yards of the 166,000 cubic yard total muck sediment contains over 10,000 ppm PCB. There are another 2,000 or 3,000 cubic yards of contaminated sand and clay beneath the most-contaminated muck sediment which will have to be excavated, some of which also contains high concentrations of PCB. Therefore, it makes sense to place the most contaminated sediments in a pocket of the proposed lagoon and cover them with less contaminated material to minimize volatilization.

A special pocket was designed in the proposed lagoon to contain contaminated material from areas A1, A2, and A3 of Slip #3.

Volatilization should be minimal if the more contaminated sediments are dredged first. The more contaminated sediments in the lagoon should be then capped with less contaminated sediments as dredging progresses. Finally, when dredging is almost finished, relatively uncontaminated Waukegan Harbor muck should be slurried to the lagoon to form a cap on the previously-dredged and settled sediments. The lower the concentration of PCB in sediment exposed to the atmosphere, the less volatilization of PCB will occur.

3.3.2 Capping the Sediments with Organic Rich Materials

The volatilization rate can be decreased to almost nothing after dredging is completed if the materials are capped with an organic rich material such as sewage treatment sludge, paper mill sludge, or carbon. Activated carbon can remove soluble PCB from lagoon water and control volatilization, but virgin material is not recommended because of the expense.

Perhaps the least costly cap that may be applied is uncontaminated muck sediments. When dredging is complete and sediments have settled in the lagoon, the dredger can be instructed as a final act to dredge relatively uncontaminated area in order that the dredge materials can form a cap on previously dredged materials. For example,

after the dredger has completed dredging sediments greater than 50 ppm (areas A1 thru A6 and B1 thru B5, he may be instructed to dredge a few thousand cubic yards from say areas C5 or C6 to form a seal on previously-dredged material.

3.3.3 Capping the Sediments with Water

Farmer (6) reports that a water column cover definitely decreases the volatilization rate of hexachlorobenzene from contaminated soils in landfills. On the other hand, Spencer (17) reports that the volatilization rate of pesticides from wet soils or water-covered soils is greater than from dry soils. Unlike PCBs and hexachlorobenzene, many pesticides can degrade to form more volatile and more water soluble daughter products.

The situation with PCBs is not clear, but a water cover should decrease volatilization rate especially if more contaminated soils or sand are covered. Under the worst roiling situations with highly-contaminated sediments, the PCB concentration in the water should not exceed 100 ppb or 150 ppb. The PCB volatilization rate from a 100 ppb solution is on the order of 50 pounds per square mile per day (using the same volatilization rates discussed earlier). On the other hand, volatilization from say 100 ppm of sand sediments may be 100 pounds per square mile per day. The volatilization rate from more contaminated sediments increases with concentration in the sediment, but the PCB concentration in the

water probably would not be much above 100 ppb (or even 200 ppb) no matter how contaminated the sediment.

The effect of a water cap on slightly-contaminated (less than say 50 ppm) sediment is not clear. If the rate in which the PCBs desorb from the sediment and solubilize in water is much less than direct volatilization from the sediment, than a water cap would be a benefit. This is probably the case with most organic rich sediments and sludges.

3.3.4 Capping the Sediments with Plastic Film

The very limited information discussed by Farmer (6) on hexachlorobenzene and the work done at Los Alamos on PCB (personal communication) suggest that PCBs can diffuse through plastic films, at least polyethylene and some of the other commercially available materials.

There may be problems with the use of plastic films at Waukegan. Among these being are (1) difficulties in applying the films over PCB-contaminated materials (2) possibilities of wind blowing the plastic films off the site, and (3) increased volatilization of PCBs caused by heat trapped beneath the film on sunny days.

Because of the potential problems and apparent lack of effectiveness, Mason & Hanger at this time does not recommend the use of plastic sheeting as a cover for contaminated sediment.

3.3.5 Capping Exposed Sediment With Dust Control Agents

There are a number of dust control formulations that are marketed for the purpose of treating soil surfaces to prevent dusting or erosion. Some polymer formulations are designed to be used with mulch (straw, paper, wood chips, etc) in order to minimize erosion on slopes during grass seeding. Mason & Hanger is not aware of any published information on the effectiveness of any of these formulations on control of PCB volatilization. However, common sense suggests that volatilization should be reduced. Mason & Hanger recommends use of a dust control material if sediment is to be exposed for more than a few weeks because of the following reasons:

- (1) application of dust control agents should minimize erosion of sediments which have deposited on the slopes of the lagoon ditches. Erosion exposes deeper, more contaminated sediments and increases the surface area of exposed sediments to the air;
- (2) Drying and dusting of exposed lagoon sediments should be prevented. Wind-blown dust containing PCBs could result in serious public alarm;
- (3) many dust control formulations have a high organic content. As discussed earlier, materials with a high organic content are less likely to volatilize PCBs or solubilize PCBs into the water;

- (4) the dust control formulation should provide an effective seal on top of the sediments minimizing drying and volatilization of PCBs from the surface.

Because of the potential for adverse public reaction to wind-blown materials, Mason & Hanger recommends that dust control formulations should not be used with light-weight surface blanket materials such as straw, mesh, or plastic films.

For this application, dust control formulations may be applied in either of two ways. One way is to topically apply an emulsion by spraying onto exposed surfaces. The surfaces should be dry enough such that the emulsion can penetrate and form a cap and not wash away to low areas of the lagoon. The second way is to mix the formulation with the incoming dredge slurry during final stages of dredging. Then the formulation will bind the settling sediments together to form a cap on previously settled sediments.

Two candidate dust control materials are the following:

- (1) Natural petroleum resin

An example is the Witco Chemical Corporation COHEREX product, which is a 60 percent petroleum emulsion in water, emulsified using a wetting agent. It is diluted with water and either sprayed onto the exposed surface or can be mixed with dredge slurry to bind the settling sediments.

(2) Synthetic polymer resin

An example is the Union Carbide dust binder concentrate 266. The synthetic polymer is proprietary, but earlier marketed Union Carbide formulations contained polyvinyl acetate and chemical modifiers, emulsified in water. The material is mixed with water before use and sprayed onto exposed surfaces. The exposed surfaces should be dry enough that the emulsified mixture can penetrate the top portion of the sediment. The material is applied at a rate of 0.01 to 0.1 gallons per square yard (as the concentrate). It can last several years without reapplication.

4.0 RECOMMENDATIONS

Every reasonable effort should be made to control volatilization during Waukegan Harbor cleanup operations. Mason & Hanger recommends the following:

- (1) The most contaminated (over 10,000 ppm PCB) sediments from locations A1, A2, and A3 of Slip #3 should be dredged first and placed in a specially-constructed compartment of the lagoon. These sediments should not be mixed with other Waukegan Harbor sediments. Dredge water, after sediments have settled in the lagoon compartments, may slop over into the lagoon proper. This dredge water is expected to contain very roughly 100 ppb of soluble PCB.
- (2) Dredging of Slip #3 should continue with the most contaminated material being dredged first. After the lagoon compartment is filled with the most contaminated material, dredge slurry water may be placed in the rest of the lagoon. As dredging progresses, less contaminated material is placed on top of more contaminated material.
- (3) During dredging of Slip #3, PCB volatilization will be the greatest from the lagoon. The PCB concentration in the water could be 100 ppb and the volatilization rate could be on the order of about 2 pounds per day. The PCB concentration in the

air just above the lagoon water could be on the order of 2 micrograms per cubic meter. There is little that can be done to reduce this volatilization other than to have this phase of the project proceed as rapidly as possible and to minimize exposure to personnel. The New York Department of Environmental Conservation recommends a maximum daily exposure to PCBs of 3 micrograms per kg of body weight. Based on a 70 kg person breathing 15 cubic meters of air per 8 hour period (heavy work), the PCB concentration in the air should not exceed 13 micrograms per cubic meter. PCB concentrations in the air and in the lagoon water (soluble PCB) should be monitored.

- (4) When dredging of Slip #3 is completed, the water in the lagoon will be recycled as the water treatment plant is being tested. The PCB concentrations in the water and ambient air should decrease during this period. These PCB concentrations should be monitored.
- (5) After the water treatment plant has been successfully demonstrated, dredging should continue. Less-contaminated sediments should be placed on top of more contaminated sediments. When dredging of all sediments above 50 ppm (areas A1 thru A6 and B1 thru B5) has been completed, the dredger should dredge some muck sediments from a relatively-uncontaminated area (say sediments under 20 ppm PCB) to form a cap on previously-dredged and lagoon-settled sediments. PCB monitoring should continue.

- (6) When dredging is complete and the lagoon is filled with sediments, excess water should be drained off and treated. Exposed sediments on the lagoon dikes and in the lagoon proper should be allowed to dry slightly (enough that the surfaces will absorb some water when rewetted). Then an emulsion-type sealer (such as Witco Chemical Corp. Coherex or Union Carbide Dust Binder Concentrate 266) should be sprayed onto exposed surfaces. This sealer should (1) minimize dusting, (2) reduce PCB volatilization, and (3) reduce erosion which would expose more-contaminated sediment.
- (7) Before excavation is to begin, as much water as possible should be drawn off and treated. The lagoon underdrain system should be opened to and in further removal of water.
- (8) Excavation can then begin. As small an area as practical should be excavated at a time to minimize volatilization of PCBs. The settled sediments on the lagoon dike slope on one side should be removed first. A ramp can then be constructed on the cleaned slope which will permit trucks and cranes to enter and remove material from the lagoon proper. PCB concentration in the air should be monitored during excavation. The lagoon underdrain system is used to remove rainwater.

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APPENDIX ITEMS

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2. New York Department of Environmental Conservation and General Electric Data on PCB Volatilization from Sediment.

General Electric Test Tank Data from Tofflemire's Paper.

Joe Soden 212 769-3120

| LOCATION | ESTIMATED CUBIC YARDS SEDIMENT | CALCULATED LBS. OF PCB |
|----------|-----------------------------------|---------------------------|
| A1 TO A6 | 7,300(MUCK) PLUS 1600(SAND)* | 250,000 |
| B1 TO B5 | 38,000 (MUCK) | 7,000 |
| C1 TO C6 | 121,000 (MUCK) | 2,200 |
| D1 TO D3 | 18,000 (MUCK) | 300 |

* May 1981 revised figures: 7,300 (muck) plus 3,700 (sand & clay)
calculated pounds of PCB revised upward to 300,000.

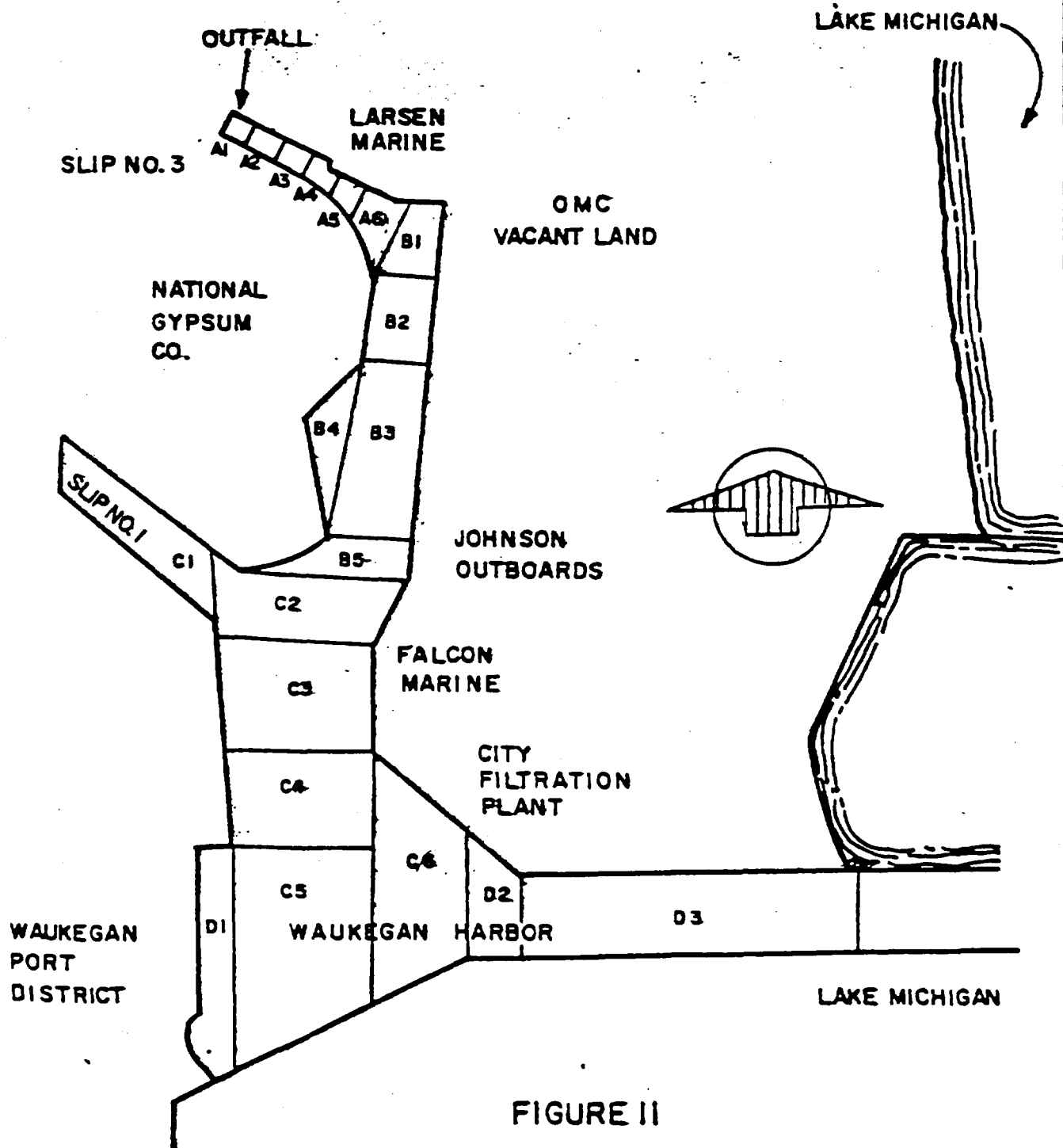


FIGURE II
EXTENT OF PCB CONTAMINATION IN
SEDIMENT IN WAUKEGAN HARBOR BY AMOUNT

New York Department of Environmental Conservation
and General Electric Data

Summary Tabulation of Air PCB Data by DEC Div. of Air Resources

(Data taken at Temperature of 65-85°F)

| <u>Site</u> | <u>Comment</u> | <u>Air PCB ug/m³</u> | <u>Sediment ug/g</u> | <u>Ratio Air/sediment</u> | <u>Reference</u> |
|--|--------------------|-------------------------------------|--------------------------|-------------------------------|--|
| Caputo Dump | Max | 300 | 10,000-50,000 | | Dr. Hawley |
| Caputo | Ave. | 130 | 10,000-50,000 | .0043 | 2/26/79 memo and original Air Resources Data |
| Ft. Miller Dump | Max | 35 | 5,000-15,000 | | |
| | Ave. | 24 | 5,000-15,000 | .0024 | |
| Remnant Area | Max | 10 | 1,000-2,000 | | |
| | Ave. | 9 | 1,000-2,000 | .006 | |
| Moreau site with excavated 3A material | Max | 15 | 600-1,000 | | |
| | Ave. | 5.6 | 600-1,000 | .007 | |
| Buoy 212 Site Summer 1979 | One sample 85°F | 0.7 | 50-100 | .0093 | Summer 1979 Air Resources Data |
| Old Moreau Site Summer 1979 | Ave. | 0.3 | 20-50 | .0085 | Summer 1979 Air Resources Data |

Summary of GE Tank Air PCB Data at 20°C

| <u>Site</u> | <u>ug/g</u> | <u>Wind speed mph</u> | <u>Air data ug/m³</u> | <u>ug/m²/hr</u> | <u>Ratio Air/sediment</u> | <u>Sediment % Finer .075 mm</u> | <u>Reference</u> |
|-------------|-------------|---------------------------|--------------------------------------|----------------------------|-------------------------------|-------------------------------------|-------------------|
| Buoy 212 | 64 | .73 | .7 | 114 | .011 | 5 | Report 55 |
| 3A Remnant | 445 | 3.6 | 3.5* | 2672* | .0079 | 32 | 1980 DEC files |
| Caputo | 20,000 | 3.6 | 70* | 47,700* | .0035 | < 2 | 1980 DEC files |

Correlation Table for 65-85°F, and Low Winds

| | | | | | |
|---------------------------|---------|--------|-------|-------|------|
| Sediment PCB ug/g | 100,000 | 10,000 | 1,000 | 100 | 10 |
| Ratio | .0020 | .0043 | .0066 | .0089 | .011 |
| Air PCB ug/m ³ | 200 | 43.0 | 6.6 | .89 | .11 |

* Data is provisional based on 1-2 samples, may change as additional data is reported by the laboratory.

Sediment to Air PCB Correlation
Low Wind and 65-85°F
Aroclor 1012/1242

